Conductivity Results. Knowing the concentration of $C(NO_2)_3^-$ from the optical absorption and also of its positive counterion which probably is a solvated proton, the equivalent conductivity of the ion pair can be calculated from the measured conductivity increase of the solutions. It turned out that the conductivity increase in pure dioxane is very low indicating a small equivalent conductivity of the ion pair in this solvent. In water–dioxane mixtures containing more than 35 mole % water, the conductivity signals were large enough to be accurately measured. Figure 5a shows a plot of the calculated equivalent conductivity *vs.* dioxane contents of the mixtures. The curve is similar in shape to the curve giving the dependence of the dielectric constant.[15] Extrapolation to 100% dioxane yields a very low value of the equivalent conductivity of less than 10 ohm^{-1} cm^2 $equiv^{-1}$. A plot of $\Lambda_{(C(NO_2)_3^-+H^+)}$ *vs.* log mole % dioxane is also shown in Figure 5b. The plot yields a straight line. The intercept of 5 ohm^{-1} cm^2 $equiv^{-1}$ on the ordinate axis at 100% dioxane is taken as the equivalent conductivity of the ion pair in this solvent. It may be pointed out that the decomposition of NO_2, produced by the reduction of TNM, to form ions is too slow ($\tau_{1/2}$ for $(NO_2)_2 \rightarrow NO_2^- + NO_3^-$ = 700 μsec[16] in water and *ca.* 10 sec in 2-propanol[9]) to affect our results.

Acknowledgment. The author wishes to express his thanks to Professor A. Henglein for many helpful discussions and for his criticism of this work.

(15) Calculated from the data in J E. Linde, Jr., and R. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).

(16) M. Grätzel, A. Henglein, J. Lilie, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **73**, 646 (1969).

The Reactions of Acetone and Hydrogen Peroxide. II. Higher Adducts[1]

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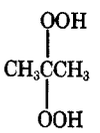
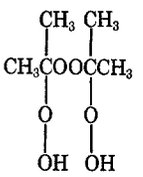
The formation of several peroxides derived from acetone and hydrogen peroxide has been investigated by proton magnetic resonance spectroscopy. The kinetics of formation of 2,2-bis(hydroperoxy)propane have been investigated in detail. The slow step was found to exhibit general acid catalysis. Values of rate constants and activation parameters are reported. A general mechanistic scheme for formation of the adducts is proposed.

Introduction

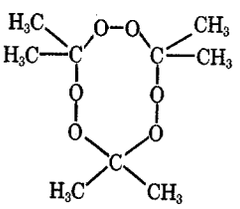
Organic peroxides derived from acetone and hydrogen peroxide have been extensively studied.[1-3] The 1:1 adduct (2-hydroxy-2-hydroperoxypropane, compound I) has recently been shown to be present in the liquid mixtures.[1,4] The following three higher adducts



II, 2,2-bis(hydroperoxy) propane



III, α,α'-bis(hydroperoxy)diisopropyl peroxide



IV, 1,1,4,4,7,7-hexamethyl-1,4,7-cyclononatriperoxane

have been identified.[2,3] Adduct II was isolated[3] (in about 12% yield) when 50% H_2O_2 was reacted with acetone at 0° and a mole ratio of 1:1 in the absence of added hydrogen ion; in the presence of hydrogen ion,

(1) (a) Abstracted from part of the Ph.D. thesis of Maria C. V. Sauer at Brown University, June 1970; (b) Paper I, M. C. V. Sauer and J. O. Edwards, *J. Phys. Chem.*, **75**, 3004 (1971).

(2) A. Rieche, *Angew. Chem.*, **70**, 251 (1958).

(3) N. A. Milas and A. Golubovic, *J. Amer. Chem. Soc.*, **81**, 6461 (1959).

(4) J. Hine and R. W. Redding, *J. Org. Chem.*, **35**, 2769 (1970), and references listed therein.

all three adducts above have been isolated with the cyclic trimer being the predominant product in concentrated solutions.

The mechanisms of formation of these different peroxides derived from acetone and hydrogen peroxide have not been investigated. Further, little is known about the equilibria between the several species. We have studied the different stages of the hydrogen peroxide–acetone interaction in (necessarily) concentrated solution by means of nmr spectroscopy. The data on primary adduct I are published elsewhere.[1b] The mechanism of formation of the higher adducts (II, III, and IV) must be different, as in these three cases replacement of OH by OOR obtains whereas formation of I occurs as an addition across the carbonyl double bond. Data on the higher adducts are presented here.

Experimental Section

General. All reagents, buffers, and equipment were the same as those reported earlier.[1] The evaluation of the equilibrium constants was also carried out as before.

Kinetics. The kinetics of formation of II were investigated as follows. The pH of the peroxide solutions was adjusted with HCl (1 *M*) in cases where buffers were not employed. The pH values were corrected for the influence of hydrogen peroxide on the glass electrode reading.[5] The ionic strength was adjusted in appropriate cases with KCl. All kinetic runs were started by adding the acetone to a known volume of peroxide solution. This operation was carried out in a separate test tube to facilitate mixing, and a small amount of the reaction mixture then was transferred to an nmr tube. A period of 10 min was allowed for temperature equilibration before points were taken.

The rate of disappearance of acetone was measured by nmr peak areas. The peak areas for both acetone and product were evaluated by the automatic integrator on the A-60A spectrometer. The concentration of acetone at any time, t, is given by the equation

$$[\text{acetone}]_t = \left(\frac{I_{Ac}}{I_{Ac} + I_p}\right)_t [\text{acetone}]_0$$

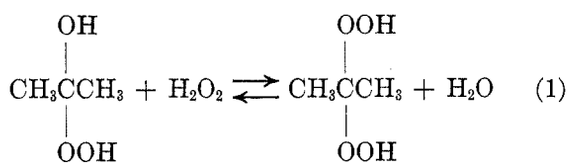
where I_{Ac} is the integrated area of the acetone peak and I_p is the area of the product peak. Brackets are used to denote concentrations, and the subscripts 0 and t refer to initial state and state at time of measurement, respectively. Values of log $[\text{acetone}]_t$ were plotted against time; from the slopes of the resultant lines, values of observed rate constants k_{obsd} were found using the equation

$$k_{obsd} = 2.303\left(\frac{\Delta(\log [\text{acetone}])_t}{\Delta t}\right)$$

Results

Stoichiometries. Each adduct exhibits a characteristic line in the methyl proton region of the nmr spectra, and identification of the lines was made by evaluation of equilibrium constants at different initial concentrations of peroxide and acetone. Adduct I, which is the 1:1 addition product, is formed very rapidly (albeit in low concentration), and it has a known nmr spectrum.[1b,4a] The spectra of freshly prepared solutions of acetone (from 3 to 10 *M*) and hydrogen peroxide (5 to 13 *M*) consist of two low-field signals at 2.23 and 1.43 δ; the 2.23 δ resonance corresponds to the methyl protons of acetone and the 1.43 δ resonance has been assigned[1,4] to adduct I.

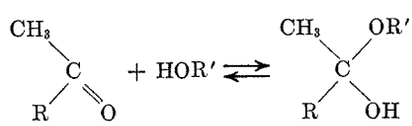
The spectra of these same solutions taken over the course of an hour after mixing show a slow decrease in the intensity of the two signals mentioned above and the appearance of a new signal which has a resonance 1 cps upfield from that of I and which quickly becomes larger than that of I. The reaction under investigation was found to be



$$\begin{matrix} \text{OH} \\ | \\ \text{CH}_3\text{CCH}_3 \\ | \\ \text{OOH} \end{matrix} + \text{H}_2\text{O}_2 \rightleftharpoons \begin{matrix} \text{OOH} \\ | \\ \text{CH}_3\text{CCH}_3 \\ | \\ \text{OOH} \end{matrix} + \text{H}_2\text{O} \qquad (1)$$

and the product can be identified (see below) as compound II previously isolated.[2,3]

Over and above the fact that a compound of this nature having the appropriate properties and analysis has been isolated and identified,[3] our assignment of the nmr line to II is based on considerable evidence. First, we observed the compound under the same conditions as it had been isolated by Milas and Golubovic.[3] The position of the methyl proton nmr line is 0.80 δ lower than that of acetone itself; this agrees with the result of Hine and Redding[4] and with the general size of the methyl proton shift observed[4] for all reactions of the type



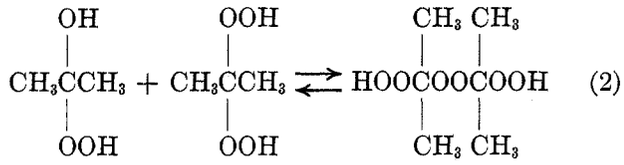
$$\begin{matrix} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \quad \| \\ \text{R} \qquad \text{O} \end{matrix} + \text{HOR}' \rightleftharpoons \begin{matrix} \text{CH}_3 \qquad \text{OR}' \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \qquad \text{OH} \end{matrix}$$

The equilibrium constants K_{II} based on a stoichiometry of one acetone and two hydrogen peroxides are constant, and no reasonable alternative structure for this composition presents itself. The values of ΔH and ΔS given below are consistent with a replacement process rather than an addition or elimination reaction. Finally, the kinetic data (rates, acid catalysis, and activation parameters) are analogous to those observed for acetal formation, and compound II may indeed be considered as a modified ketal.

Compound II is the dominant product (as indicated by the size of the nmr signal) when the ratio $[\text{acetone}]/[\text{H}_2\text{O}_2]$ is equal to or less than 0.07. In those experiments where this ratio is greater than 0.07, a third ad-

(5) J. R. Kolczinski, E. M. Roth, and E. S. Shanley, *J. Amer. Chem. Soc.*, 79, 531 (1957).

duct which is apparently the reaction product derived from condensation of adducts I and II is formed.



(2)

This product, denoted III, is α,α'-bis(hydroperoxy)diisopropyl peroxide and is observed in the nmr spectra as a signal at 3 cps lower field from that of II.

On further increasing the acetone concentration, ([acetone]/[H_2O_2]) > $^1/_6$, a fourth resonance which we assign to cyclic adduct IV is observed after several days. In solutions where the ratio [acetone]/[H_2O_2] is about unity, the spectra taken 24 hr after the mixing of the reactants indicate the presence of all four products with the 2-hydroxy-2-hydroperoxypropane resonance as a shoulder on the 2,2-bis(hydroperoxy)propane resonance.

Equilibrium Constants. To prove the stoichiometry of the reactions that lead to the formation of 2,2-bis(hydroperoxy)propane and α,α'-bis(hydroperoxy)diisopropyl peroxide, the spectra of several solutions were taken at equilibrium over a range of acetone concentrations from 0.5 to 6 M, of hydrogen peroxide concentration from 9 to 15 M, and of water concentration from 20 to 40 M. The resonances were integrable by planimeter or, in some cases of very good resolution, with the automatic integrator of the spectrometer. The equilibrium constants K_{II} and K_{III} were calculated using the relationships

$$K_{II} = \frac{[II][H_2O]}{[I][H_2O_2]} \qquad K_{III} = \frac{[III][H_2O]}{[I][II]}$$

$$[I]_e = K_I[\text{acetone}]_e[H_2O_2]_e$$

$$[H_2O_2]_e = [H_2O_2]_0 - [I] - 2[II] - 3[III]$$

$$[H_2O]_e = [H_2O]_0 + [II] + 2[III]$$

Values for the equilibrium constants K_{II} and K_{III} at several temperatures are given in Table I. Every constant therein reported represents an average of at least four determinations; at 40°, each K_{II} value represents an average of five runs in the absence of compound III and five runs in the presence of compound III. Table II shows the thermodynamic parameters obtained for each reaction.

Table I: Equilibrium Constants[a] for the Formation of 2,2-Bis(hydroperoxy)propane and α,α'-Bis(hydroperoxy)diisopropyl Peroxide

Temp, °C	K_{II}	K_{III}
5	114 ± 8	44 ± 4
25	170 ± 8	62 ± 8
32	180 ± 8	67 ± 6
40	218 ± 12	78 ± 6

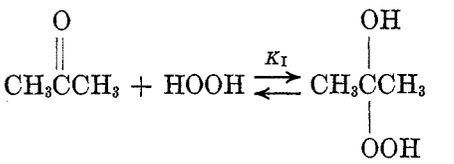
[a] For the definitions of K_{II} and K_{III}, see text.

Table II: Thermodynamic Parameters[a] for the Formation of 2,2-Bis(hydroperoxy)propane and α,α'-Bis(hydroperoxy)diisopropyl Peroxide at 25°

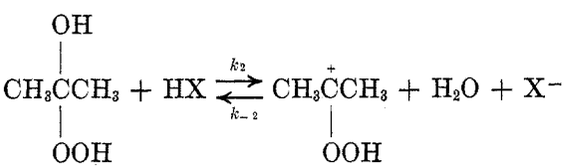
Adduct	$\Delta H°$	$\Delta S°$	$\Delta G°$	$T\Delta S°$
2,2-Bis(hydroperoxy)propane	3.2	21	−3.0	6.2
α,α'-Bis(hydroperoxy)diisopropyl peroxide	2.9	18	−2.4	5.3

[a] The units for $\Delta H°$, $\Delta G°$, and $T\Delta S°$ are kcal mol^{-1} and for $\Delta S°$ are cal mol^{-1} deg^{-1}. The standard deviations are estimated to be about 0.3 for $\Delta H°$, $\Delta G°$, and $T\Delta S°$ and about 1 for $\Delta S°$.

Kinetics of Adduct II Formation. To explain the formation of the 2,2-bis(hydroperoxy)propane, the following mechanism was initially hypothesized.



(3)



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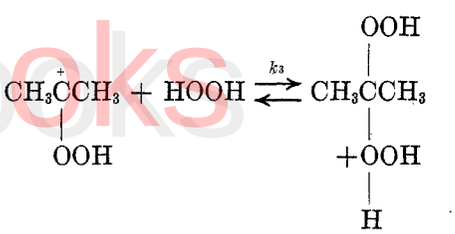

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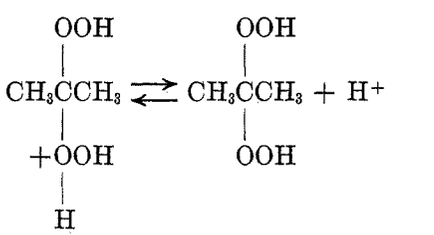

(6)

Different rate laws were derived assuming first step 4 and then step 5 to be the rate-determining step of the reaction. When step 4 is rate determining, the rate law should be

$$\frac{-\mathrm{d}[\text{acetone}]}{\mathrm{d}t} = \frac{k_2K_I[\text{acetone}][H_2O_2][HX]}{1 + K_I[H_2O_2]} \quad (7)$$

with the denominator having a value near to unity. When step 5 is rate determining, the rate law should be

$$\frac{-\mathrm{d}[\text{acetone}]}{\mathrm{d}t} = \left(\frac{k_2}{k_{-2}}\right)\left(\frac{k_3K_I[\text{acetone}][H_2O_2]^2[H^+]}{1 + K_I[H_2O_2]}\right) \quad (8)$$

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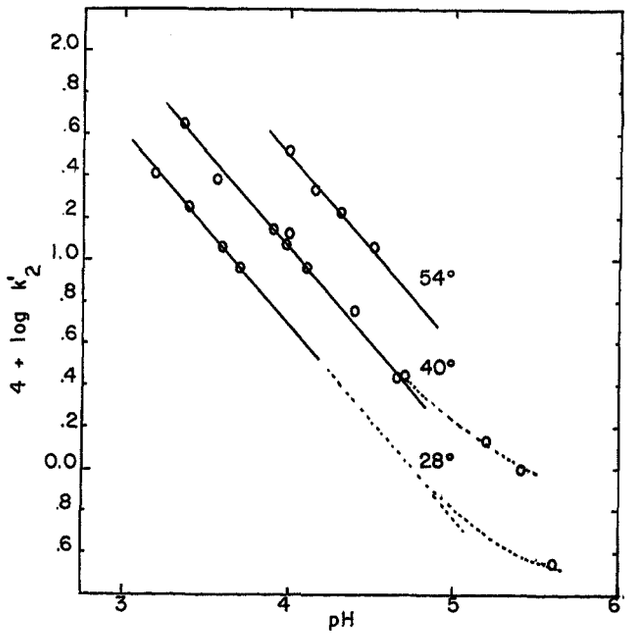


Figure 1. Dependence of rate constant k_2' (as defined in text) on pH at three temperatures.

A significant difference lies in the nature of catalysis by acid: for the first mechanism general acid catalysis is predicted, whereas for the second specific acid catalysis is predicted.

The dependence of the reaction on hydrogen peroxide concentration was studied at 24°, at constant pH and in the absence of any other acid. It was found that the rate law followed by the reaction is the same as the law derived assuming step 4 as the rate-determining step, that is

$$k_{obsd}(1 + K_I[H_2O_2]) = k_2'K_I[H_2O_2]$$

where k_{obsd} is the first-order-pseudo constant for decrease in acetone concentration. The reaction was found to be catalyzed by both H^+ and undissociated acids, and eq 9 shows the observed dependence

$$k_2' = k_0 + k_H[H^+] + k_a[HX] \quad (9)$$

Dependence of the rate constant k_2' on pH at three different temperatures is shown in Figure 1.

At low pH and in the absence of any molecular acid the reaction proceeds largely *via* the path involving catalysis by the solvated proton. Thus, for these data, $k_2' = k_H[H^+]$, and the slope of -1 is observed as expected at pH values lower than 5. A "spontaneous" reaction was observed in the region where the amount of proton catalysis becomes unimportant (pH >5). This spontaneous reaction can be attributed to catalysis by hydrogen peroxide and water. The rate constants k_H and k_0 can be obtained by plotting k_2' against $[H^+]$ (Figure 2) according to the equation

$$k_2' = k_0 + k_H[H^+] \quad (10)$$

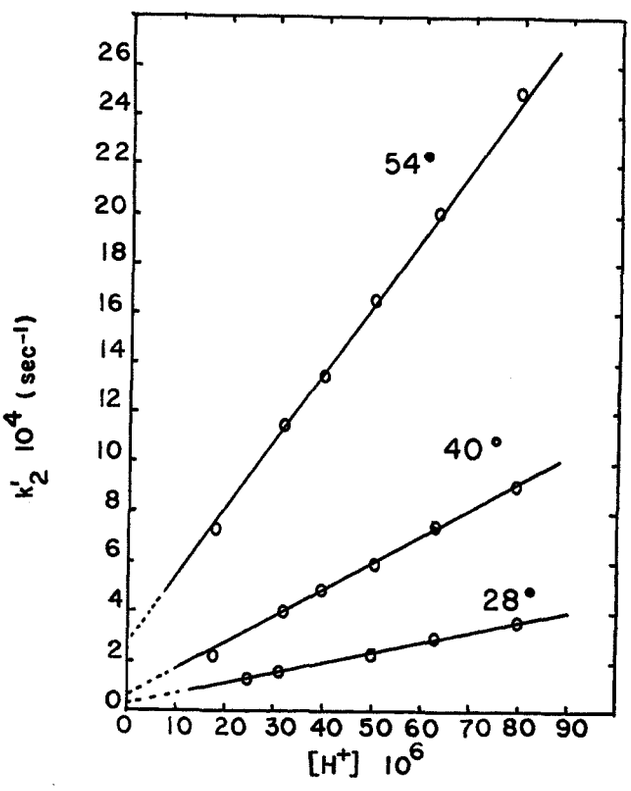


Figure 2. Separation of rate constant k_2' into k_0 and k_H terms (see eq 9) at three temperatures.

The slope of the line is equal to k_H, and the constant k_0 is obtained from the intercept by extrapolation to $[H^+] = 0$. Values of k_H and k_0 at three different temperatures are listed in Table III.

Table III: Proton-Catalyzed and Spontaneous Rate Constants of Formation of 2,2-Bis(hydroperoxy)propane at Three Temperatures

Temp, °C	k_H, M^{-1} sec^{-1}	$k_0 \times 10^4$, sec^{-1}
28	4.25	0.30
41	10.5	0.85
54	27.6	2.70

Table IV: Acid Catalytic Rate Constants at 40° and $\mu = 1$ for the Formation of 2,2-Bis(hydroperoxy)propane

Acid	p^a	q^a	pK_a	k_a, M^{-1} sec^{-1}
H_3O^+	3	1	−1.74	10.5
Cl_3CCOOH	1	2	+0.66	2.00
$Cl_2CHCOOH$	1	2	+1.31	4.5×10^{-1}
HSO_4^-	1	2	+1.52	35×10^{-2}
H_3PO_4	3	2	+1.78	13.9×10^{-2}
$ClCH_2COOH$	1	2	+2.76	2.1×10^{-2}

[a] These are the statistical corrections in the Brönsted equation $k_a/p = G_a((q/p)K_a)^\alpha$.

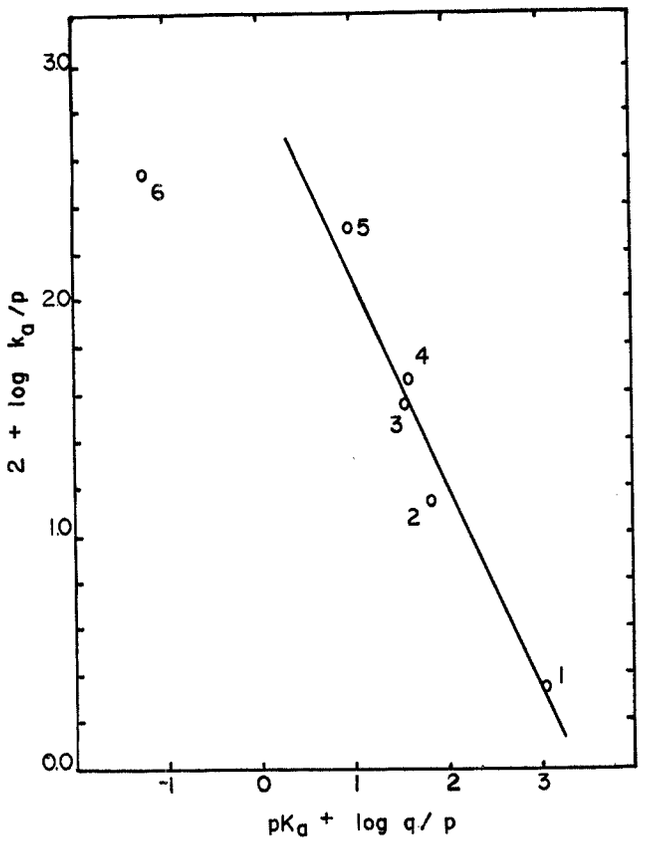


Figure 3. Variation of acid-catalyzed rate constant k_a with pK_a of the corresponding general acid. This Brönsted plot has data for (1) $ClCH_2COOH$, (2) H_3PO_4, (3) HSO_4^-, (4) $Cl_2CHCOOH$, (5) Cl_3CCOOH, and (6) H_3O^+.

At constant pH and working with increasing concentrations of XH, it is possible to obtain the corresponding acid catalytic constant k_a by use of eq 9. Values of k_a for five different acids are listed in Table IV. A Brönsted plot of the system is shown in Figure 3.

Activation parameters of the reaction were calculated for both types of reactions and are listed in Table V. In this case the overall entropies of activation are equal to

$$\Delta S_1^{\pm} = \Delta S_1^{\circ} + \Delta S_H^{\pm} \text{ (H}^+\text{-catalyzed reaction)}$$

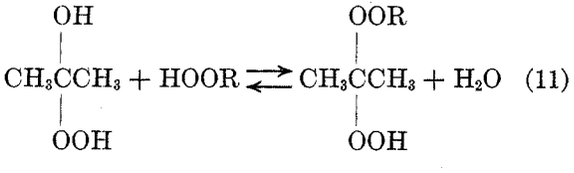
and

$$\Delta S_2^{\pm} = \Delta S_1^{\circ} + S_0^{\pm} \text{ (spontaneous reaction)}$$

where ΔS_1° is the change in entropy of the rapid equilibrium step (eq 3) prior to the rate step.

Discussion

General Pathway. The formation reactions of adduct II and adduct III are similar to each other as may be visualized from the general equation



(11)

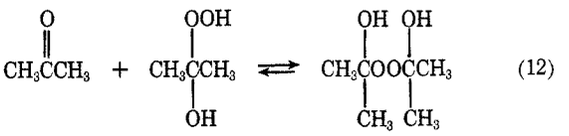
Table V: Activation Parameters[a] at 25° for the Formation of 2,2-Bis(hydroperoxy)propane

	E_a	$\Delta H^{\pm}$	$\Delta S^{\pm}$	$\Delta S^{\pm} - \Delta S_1^{\circ}$
"Spontaneous" reaction	17.5	16.9	−22	6
H^+-catalyzed reaction	13.8	13.2	−10	18

[a] Units for E_a and $\Delta H^{\pm}$ are kcal mol^{-1}, and for $\Delta S^{\pm}$ and $\Delta S^{\pm} - \Delta S_1^{\circ}$ are cal mol^{-1} deg^{-1} The standard deviations for E_a and $\Delta H^{\pm}$ are estimated as 0.3, whereas for $\Delta S^{\pm}$ and $\Delta S^{\pm} - \Delta S_1^{\circ}$ they are 1.

Both reactions involve the replacement of an OH group by an OOR group with concurrent formation of water. For adduct II, HOOR represents hydrogen peroxide; for adduct III, HOOR represents adduct II itself. The similarity in the chemistry of these two reactions is reflected in the similarity of the thermodynamic parameters.

All of the products from the reaction of acetone and hydrogen peroxide can be formed by the steps of eq 1, 2, 3 plus the following



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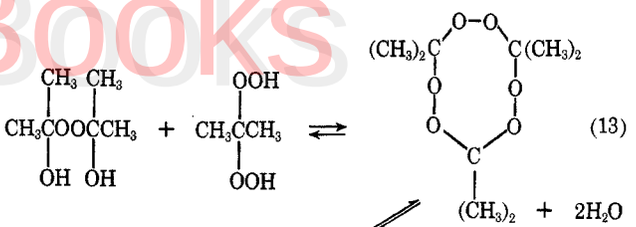

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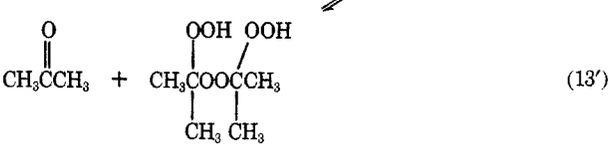

(13′)

Only two general types of stoichiometry are necessary for the description of products from the reactions of hydroperoxides ROOH and carbonyl compounds R′C(=O)R″. These two types are addition of ROOH across the double bond (such as in eq 3) and conversion of COR‴ to COOR as in eq 11. Although the details vary from adduct to adduct, the general pathways should be related.

Stage 12 was not observed by the nmr technique. The product of this reaction should be present in smaller quantity than adduct I as the acetone concentration is small. The equilibrium constants obtained for formation of adduct I would have shown deviations from constancy if the process were important; no such deviations were observed.

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Cyclic adduct IV could result from either of the two steps proposed (eq 13 and 13′) or from some related process. The complexity of the stoichiometry coupled with the fact that adduct IV can under some circumstances be the predominant product (90%) strongly suggests that the other adducts are intermediates in the formation of this stable cyclic peroxide.

Mechanism of Formation of 2,2-Bis(hydroperoxy)propane. According to the results obtained for (a) dependence of rate on peroxide concentration, (b) pH dependence of the rate, (c) general acid catalysis of the rate, and (d) activation parameters, it can be concluded that the mechanism of formation of 2,2-bis(hydroperoxy)-propane is indeed that described in the Results section. The probable steps are (3), (4), (5), and (6) with (4) being the rate-determining step.

The Brönsted law applied to our system is represented in Figure 3. The slope of the line is 0.8, with a negative deviation for H_3O^+. The observed spontaneous reaction is mainly attributed to catalysis by hydrogen peroxide ($pK_a = 11.4$)[6] which is present in a considerable concentration; this cannot, however, be considered as proved.

The activation parameters reflect the changes from ground state to transition state. The entropy of adduct I formation is -28 cal mol^{-1} deg^{-1}, and the observed activation entropies $\Delta S^{\ddagger}_{obsd}$ must be corrected for this contribution. The remnant values $\Delta S_H^{\ddagger}$ and $\Delta S_0^{\ddagger}$ are $+18$ and $+6$ cal mol^{-1} deg^{-1}, respectively. These are for the processes

$$\mathrm{I} + \mathrm{H_3O^+} \longrightarrow \mathrm{CH_3\overset{+}{C}(OOH)CH_3} + 2\mathrm{H_2O}$$

and

$$\mathrm{I} + \mathrm{H_2O_2} \longrightarrow \mathrm{CH_3\overset{+}{C}(OOH)CH_3} + \mathrm{H_2O} + \mathrm{OOH^-}$$

These activation entropies, although most certainly complicated as to contributing influences,[7,8] seem to be dominated by the entropy increase resulting from the increase in number of particles.

The reaction of eq 1 is analogous to the formation of an acetal from a hemiacetal, which process is known to be catalyzed by acid. Both general acid catalysis and specific acid catalysis[9-13] have been reported. Therefore, the general acid catalysis found here is unusual, albeit unexceptional.

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